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(71)Applicant : KYOCERA CORP

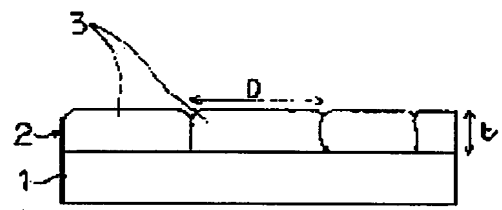
(72)Inventor : NAGAKARI HISANORI

(54) THIN DIELECTRIC FILM AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thin dielectric film having both of higher relative dielectric constant and higher insulation and a manufacturing method thereof.

SOLUTION: In a thin dielectric film 2 having a thickness of 0.3-2 μm consisting of perovskite-type crystal grains 3 containing Pb, Mg, Nb and Ti as metal elements, the perovskite-type crystal grain 3 has a grain diameter D and the film consists of flat grains 3 whose average diameter d is larger than the film thickness t. Here, the thin dielectric film 2 has a relative di lectric constant not less than 250 and a breakdown voltage not less than 60 V/μm at frequency 1 kHz (at room t mperature) for measurement.



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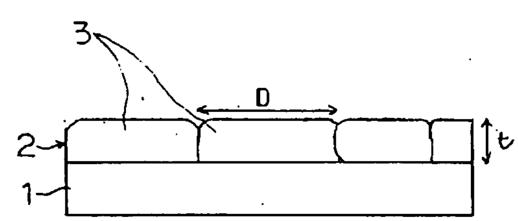
(71)出願人　000006633
京セラ株式会社
京都府京都市伏見区竹田鳥羽殿町６番地

(72)発明者　永仮　尚謙
鹿児島県国分市山下町１番４号　京セラ株式会社総合研究所内

(54)【発明の名称】　誘電体薄膜およびその製法

(57)【要約】
【課題】高い比誘電率と高い絶縁性を兼ね備えた誘電体薄膜およびその製法を提供する。
【解決手段】金属元素としてＰｂ、Ｍｇ、ＮｂおよびＴｉを含むペロブスカイト型結晶粒子３からなる膜厚０．３～２μｍの誘電体薄膜２であって、ペロブスカイト型結晶粒子３が、その平均粒径ｄが膜厚ｔよりも大きい偏平粒子３からなるものである。ここで、誘電体薄膜２は、測定周波数１ｋＨｚ（室温）での比誘電率が２５００以上、絶縁破壊電圧が６０Ｖ／μｍ以上であることが望ましい。



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【特許請求の範囲】

【請求項１】金属元素としてＰｂ、Ｍｇ、ＮｂおよびＴｉを含むペロブスカイト型結晶粒子からなる膜厚０．３～２μｍの誘電体薄膜であって、前記ペロブスカイト型結晶粒子が、その平均粒径ｄが膜厚ｔよりも大きい偏平粒子からなることを特徴とする誘電体薄膜。

【請求項２】測定周波数１ｋＨｚ（室温）での比誘電率が２５００以上、絶縁破壊電圧が６０Ｖ／μm以上であることを特徴とする請求項１記載の誘電体薄膜。

【請求項３】溶媒として２価アルコールを用い、かつ他の求核性を有する有機金属化合物の存在下においても安定なＭｇ－Ｏ－Ｎｂ結合を有するＭｇＮｂ複合アルコキシド分子を用いて、Ｐｂ、Ｍｇ、ＮｂおよびＴｉを含むペロブスカイト型複合酸化物の前駆体溶液を作製し、この前駆体溶液を基板上に０．３～０．７５μｍの厚みで塗布し、熱処理し、焼成することを特徴とする誘電体薄膜の製法。

【請求項４】２価アルコールは、１，３－プロパンジオール、１，３－ブタンジオール、２，４－ペンタンジオールであることを特徴とする請求項３記載の誘電体薄膜の製法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は誘電体薄膜およびその製法に関し、特にＤＲＡＭ、デカップリングコンデンサに利用可能な薄層コンデンサの誘電体薄膜並びにその製法に関するものである。

【０００２】

【従来技術】近年、電子機器の小型化に伴い、電子部品の小型化、薄膜化が要求されている。なかでも、コンデンサの小型大容量化は必要不可欠となっている。

【０００３】従来、薄膜コンデンサ材料としてゾルゲル法、スパッタ法、ＣＶＤ法等の成膜法を用いてTa_2O_5や$SrTiO_3$、（Ｂａ、Ｓｒ）TiO_3が主に研究されているが、これら材料の比誘電率は小さいため、小型大容量の薄膜コンデンサを実現するのは困難であった。そこで、これら小型大容量の薄膜コンデンサを実現する為に、大きな比誘電率および良好な温度特性を有する$Pb(Mg_{1/3}Nb_{2/3})O_3$（以下ＰＭＮということもある。）等に代表されるペロブスカイト型複合酸化物の薄膜化が試みられているが、室温での比誘電率が２０００以上の薄膜材料は得られていないのが現状であった。

【０００４】

【発明が解決しようとする課題】しかしながら、誘電体薄膜の絶縁性は比誘電率の増大とともに、小さくなる傾向があり、高い比誘電率を示す誘電体膜の絶縁性は一般的に小さいと考えられていた。つまり、高い比誘電率と高い絶縁性を兼ね備えた誘電体薄膜材料は得難いものであった。

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【０００５】また、上記薄膜形成方法ではクラック発生等の問題で、薄膜コンデンサを作製する手法としては成膜効率が低いため実用性に乏しいという問題点があった。

【０００６】本発明は、高い比誘電率と高い絶縁性を兼ね備えた誘電体薄膜およびその様な誘電体薄膜を容易に得ることができる製法を提供することを目的とする。

【０００７】

【課題を解決するための手段】本発明の誘電体薄膜は、金属元素としてＰｂ、Ｍｇ、ＮｂおよびＴｉを含むペロブスカイト型結晶粒子からなる膜厚０．３～２μｍの誘電体薄膜であって、前記ペロブスカイト型結晶粒子が、その平均粒径ｄが膜厚ｔよりも大きい偏平粒子からなるものである。誘電体薄膜は、測定周波数１ｋＨｚ（室温）での比誘電率が２５００以上、絶縁破壊電圧が６０Ｖ／μm以上であることが望ましい。

【０００８】また、本発明の誘電体薄膜は、溶媒として２価アルコールを用い、かつ他の求核性を有する有機金属化合物の存在下においても安定なＭｇ－Ｏ－Ｎｂ結合を有するＭｇＮｂ複合アルコキシド分子を用いて、Ｐｂ、Ｍｇ、ＮｂおよびＴｉを含むペロブスカイト型複合酸化物の前駆体溶液を作製し、この前駆体溶液を基板上に０．３～０．７５μｍの厚みで塗布し、熱処理し、焼成することにより作製される。ここで、２価アルコールは、１，３－プロパンジオール、１，３－ブタンジオール、２，４－ペンタンジオールであることが望ましい。

【０００９】

【作用】本発明の誘電体薄膜では、測定周波数１ｋＨｚ（室温）での比誘電率が２５００以上、絶縁破壊電圧が６０Ｖ／μｍ　以上の特性を達成できる。これは、誘電体層を構成する結晶粒子が、平均粒径（ｄ）と膜厚（ｔ）の比がｄ／ｔ＞１．０となるような偏平粒子形状になるため、粒径の大きいバルク体の特徴である高い比誘電率を発現すると同時に、薄膜面内において粒界の数が減少するため、膜絶縁性を向上できるためである。また、本発明の誘電体薄膜は、測定周波数１００ＭＨｚにおいても、比誘電率が２０００以上の特性を有し、高周波領域においても比誘電率が高いものである。

【００１０】そして、本発明の誘電体薄膜は、ＭｇＮｂ複合アルコキシド分子を合成する際、２価アルコール溶媒中において、Ｍｇ及びＮｂの金属化合物間の反応促進、及び複合アルコキシド分子を安定化する手法を用い、他の求核性有機金属化合物の存在下においても、安定なＭｇ－Ｏ－Ｎｂ結合を有するＭｇＮｂ複合アルコキシドを合成させ、このＭｇＮｂ複合アルコキシド分子を含む粘度の高い溶液を用い、粘度の高い$Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$前駆体溶液を合成し、この前駆体溶液を０．３～０．７５μｍの厚みで基板上に塗布し、熱処理した後、焼成することにより、本発明の誘電体薄膜を容易に得ることができる。

【００１１】本発明の誘電体薄膜における高い比誘電率は、結晶粒子の偏平構造による因子の他に、塗布溶液中の前駆体分子の構造にも起因する。

【００１２】溶液の段階で既にコランバイト（$MgNb_2O_6$）に近い構造を持つ、強固なＭｇ－Ｏ－Ｎｂ結合を有するＭｇＮｂ複合アルコキシド分子が形成されているため、他の求核性有機金属化合物（例えば酢酸鉛）に対して安定であり、Ｍｇ－Ｏ－Ｎｂ結合が破壊されることなく、$Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$前駆体が形成されるため、高い比誘電率が実現される。

【００１３】また、本発明の誘電体薄膜における偏平粒子は、塗布溶液の粘度増加により成膜１回当りの膜厚が増大した為、生成する。これは、塗布膜厚の増大のために、その膜中に存在する前駆体の濃度が高くなり、成膜１回当り０．３～０．７５μｍの膜厚が形成可能となると同時に、結晶化後の粒成長が膜面内で発生し、上記に示した膜厚に対して粒径の大きい偏平粒子として成長するからである。また、偏平粒子の生成により、結晶粒界の数が減少するため、絶縁破壊電圧６０Ｖ／μｍという高い絶縁性を有する誘電体薄膜を得ることが可能となる。

【００１４】

【発明の実施の形態】本発明の誘電体薄膜は、偏平粒子から構成されることを特徴とする。図１は、基板１上に誘電体薄膜２を形成した状態を示す断面図、図２はその平面図を示しており、膜厚ｔの誘電体薄膜２に粒径Ｄの粒子３が存在している。ここで、平均粒径（ｄ）と膜厚（ｔ）の比ｄ／ｔが１．０より大きい場合を偏平粒子３として定義した。本発明の誘電体薄膜では、比誘電率および絶縁抵抗向上のためには、ｄ／ｔが２以上、特に４以上の偏平粒子３からなることが望ましい。

【００１５】本発明の誘電体薄膜作製においては、まず塗布溶液としてＰｂ、Ｍｇ、Ｎｂ、Ｔｉの有機金属化合物が均一に溶解した前駆体溶液を調製する。

【００１６】まずＭｇ、及びＮｂの有機酸塩、無機塩、アルコキシドから選択される少なくとも１種のＭｇ化合物、Ｎｂ化合物を、Ｍｇ：Ｎｂ＝１：２のモル比で$R(OH)_2$、Ｒ：炭素数３以上のアルキル基）で示される２価のアルコール溶媒に混合する。

【００１７】混合後、還流操作を行い、他の求核性の有機金属化合物の存在下においても安定なＭｇ－Ｏ－Ｎｂ結合を有するＭｇＮｂ複合アルコキシド分子を合成する。

【００１８】この時、炭素数２のエチレングリコールを溶媒として用いると、溶媒の架橋効果が促進され、白濁・ゲル化が生じてしまう。塗布溶液の安定性を重視するためには２価アルコール溶媒分子の分子構造が重要であり、分子内において、１，３および２，４位置に水酸基を有し、合成したＭｇＮｂ複合アルコキシド分子とのアルコール交換反応により、６員環構造をとり、安定化効果を有するような、１，３－プロパンジオール、１，３－ブタンジオール、２，４－ペンタンジオール等の溶媒を選択する事が望ましい。

【００１９】また安定なＭｇ－Ｏ－Ｎｂ結合を有するＭｇＮｂ複合アルコキシド分子を得るには、以下のような方法がある。（１）Ｍｇのカルボン酸塩とＮｂのアルコキシドとの還流操作により、分子内での脱エステル反応を促進する方法。（２）ＭｇおよびＮｂのアルコキシド原料を溶媒に混合し、溶媒の沸点まで溶液の温度を上昇させ、還流操作による複合化を行った後、無水酢酸、エタノールアミン、アセチルアセトン等に代表される安定化剤を添加する方法。（３）Ｍｇの水酸化物とＮｂのアルコキシド、あるいはＭｇのアルコキシドとＮｂの水酸化物の還流操作により、分子内での脱アルコール反応を促進する。

【００２０】以上のいずれかの手法を用いる事により、他の求核性有機金属化合物の存在下においても安定なＭｇ－Ｏ－Ｎｂ結合を有するＭｇＮｂ複合アルコキシド分子を合成できるが、これらのうちでも、（１）の方法が特に望ましい。

【００２１】次に鉛（Ｐｂ）の有機酸塩、無機塩、アルコキシドから選択される少なくとも１種の鉛化合物を上記Ｍｇ－Ｎｂ複合溶液に混合し、Ｐｂ：（Ｍｇ＋Ｎｂ）＝１：１のモル比からなるPMN塗布溶液とする。この時、Ｐｂを数%過剰にしても良い。

【００２２】さらに溶液の粘度を上げる場合は、９０℃から１００℃での加熱重合操作を行ってもよい。この加熱重合により、数１００ｃＰ以上の高い溶液粘度を有する塗布溶液を得る事ができる。

【００２３】$PbTiO_3$（ＰＴ）前駆体溶液は鉛（Ｐｂ）の有機酸塩、無機塩、アルコキシドから選ばれる少なくとも１種の鉛化合物とチタン（Ｔｉ）の有機酸塩、無機塩、アルコキシドから選ばれる少なくとも１種のチタン化合物と、２価アルコール溶媒とを混合し、還流操作を行う事によって得られる。この場合、溶液粘度は５０ｃＰ～１００ｃＰの溶液を得ることができる。

【００２４】PMN－ＰＴ前駆体溶液は先に合成したＰMN前駆体溶液とＰＴ前駆体溶液を混合する事によって得られる。混合した後の溶液粘度はPMN溶液の粘度にもよるが、溶液粘度７０ｃＰから約１２００ｃＰである。

【００２５】これら作製したPMN－ＰＴ塗布溶液を用いて、下部電極の形成された基板上にスピンコート法、ディップコート法、スプレー法等の手法により成膜する。

【００２６】成膜後、１００℃以下の温度で乾燥を行った後、３００℃～４００℃の温度で熱処理を行い、膜中に残留した有機物を燃焼させ、ゲル膜とする。１００℃以下の乾燥工程はゲル膜の段階でクラック発生を防止する為に必要である。

【００２７】得られたクラックのないゲル膜を７５０℃～８５０℃で焼成を行い、結晶質の誘電体薄膜が作製される。得られた誘電体薄膜の膜厚は使用した溶液の粘度および成膜条件にもよるが、成膜１回当り０．３～０．７５μｍである。さらに層厚みを大きくする場合は成膜操作を繰り返す。しかし、焼成後のクラック発生を抑制するために、焼成後膜厚が２．０μｍ以下であることが必要である。また、絶縁特性を考慮すると、誘電体層内の結晶粒子は、粒径が０．５～２μｍの偏平粒子から構成される組織の方が望ましい。

【００２８】本発明の薄膜コンデンサは、例えば、Ｐｔ、Ａｕ、Ｃｒ、Ｎｉ、Ｃｕ等をアルミナ、サファイア、Ｓｉ等から選ばれる基板上にスパッタ法、蒸着法、グラビア印刷等の手法により成膜して下部電極を形成する。この時、基板の表面粗さには特に制限はないが、電極－基板界面での膨れによる膜のクラック発生を防止する為に、電極－基板間の密着性を向上させる事が重要である。

【００２９】この下部電極膜の表面に、上記誘電体膜を上記方法で成膜して形成し、この後に誘電体薄膜表面に下部電極と同様にして上部電極を成膜することにより得られる。また、積層コンデンサは誘電体層と電極とを交互に積層することにより得られる。

【００３０】

【実施例】

実施例１

酢酸ＭｇとＮｂエトキシドを１：２のモル比で秤量し、１，３－プロパンジオール中で還流操作（１２４℃で６時間）を行い、ＭｇＮｂ複合アルコキシド溶液（Ｍｇ＝５ｍｍｏｌ、Ｎｂ１０ｍｍｏｌ、１，３－プロパンジオール１５０ｍｍｏｌ）を合成した。次に酢酸鉛３水和物１５ｍｍｏｌをモル比Ｐｂ：（Ｍｇ＋Ｎｂ）＝１：１になるよう混合し、６０℃で２５分加熱する事により溶解させ、PMN溶液を合成した。

【００３１】イソプロポキシＴｉ（１５ｍｍｏｌ）と酢酸Ｐｂ（無水物）をモル比Ｐｂ：Ｔｉ＝１：１になるように１，３－プロパンジオールに混合し、還流操作を行い、$PbTiO_3$（ＰＴ）溶液を合成した。

【００３２】合成したＰＭＮ前駆体溶液とＰＴ前駆体溶液とモル比がPMN：PT＝０．９：０．１になるよう混合し、溶液粘度１３０ｃＰのPMN－ＰＴ塗布溶液（溶液Ａ）とした。

【００３３】塗布溶液Ａを９０℃で加熱重合させ、溶液粘度３００ｃＰ（溶液Ｂ）、溶液粘度５６０ｃＰ（溶液Ｃ）をそれぞれ合成した。

【００３４】電極となるＰｔ（１１１）が６５０℃でスパッタ蒸着されたサファイア単結晶基板およびアルミナ基板上の上記Ｐｔ電極の表面に、前記３種の塗布溶液（溶液Ａ、Ｂ、Ｃ）をスピンコーターで、２５００ｒｐｍ．、３３００ｒｐｍ．、５０００ｒｐｍ．の成膜条件でそれぞれ塗布し、乾燥させた後、３００℃で熱処理を行い、クラックのないゲル膜を作製した。その後、８３０℃で３分間（大気中）の焼成を行った。また、成膜１回後、クラックが発生しなかった試料に限り、２回および３回、前述の操作を繰り返し、膜厚を厚くした試料も作製した。

【００３５】この後、ＬＣＲメーター（ヒュウレットパッカード社製ＨＰ４２８４Ａ）を用いて、薄膜コンデンサの静電容量を測定し、比誘電率を求めた。絶縁破壊電圧はピコアンペアメーター（ヒュウレットパッカード社製ＨＰ４１４０Ｂ）を用いて、０Ｖから１００Ｖの直流電圧を印加して、リーク電流値が1×10^{-3}Ａ以上となった時点を絶縁破壊として評価した。平均粒径（ｄ）は薄膜表面のＳＥＭ観察写真より、インターセプト法を用いて算出した。また、膜厚（ｔ）は薄膜の断面ＳＥＭ観察写真より算出した。これらの結果を表１に記載した。

【００３６】

【表１】

試料No.	溶液No.	溶液粘度(cP)	成膜条件(rpm.)	塗布膜厚μm/回	塗布回数	膜厚t μm	平均粒径d μm	d/t	比誘電率	絶縁破壊電圧V/μm	備考
1	A	130	5000	0.30	1	0.30	3.3	11.0	3100	85	
2	A	130	6000	0.30	2	0.63	3.6	5.7	3200	80	
3	A	130	5000	0.30	3	0.9	3.8	4.2	3100	75	
4	A	130	3300	0.4	1	0.4	2.5	6.3	3000	77	
5	A	130	3300	0.4	2	0.8	2.8	3.5	3100	70	
6	A	130	3300	0.4	3	1.2	3.0	2.5	3100	70	
7	A	130	2500	0.65	1	0.65	1.4	2.2	2700	67	
8	A	130	2500	0.65	2	1.2	1.8	1.5	2700	65	
9	A	130	2500	0.65	3	2.0	2.3	1.2	2800	65	
10	B	300	5000	0.4	1	0.4	2.5	6.3	3000	75	
11	B	300	5000	0.4	2	0.7	2.8	4.0	3100	75	
12	B	300	5000	0.4	3	1.15	3.1	2.7	3000	70	
13	B	300	3300	0.6	1	0.6	2.1	3.5	3050	70	
14	B	300	3300	0.6	2	1.15	2.4	2.1	3100	65	
15	B	300	3300	0.6	3	1.7	2.6	1.5	3100	60	
16	C	560	5000	0.55	1	0.55	1.2	2.2	2700	67	
17	C	660	5000	0.55	2	1.0	1.4	1.4	2600	65	
18	C	560	5000	0.55	3	1.45	1.6	1.1	2700	60	
19	C	560	3300	0.75	1	0.75	1.2	1.6	2800	65	
20	C	560	3300	0.75	2	1.3	1.5	1.2	2800	60	
*21	C	660	3300	0.75	3	2.1	2.3	1.2	・・・		ｸﾗｯｸ
*22	D	6	3300	0.09	10	0.9	0.4	0.44	2000	45	
*23	E	2	3300	0.04	20	0.8	0.3	0.38	1800	40	
*24	D	6	3300	0.09	4	0.36	0.2	0.56	1900	50	
*25	D	6	3300	0.09	3	0.27	0.15	0.56	1800	47	

＊印は本発明の範囲外の試料を示す。

【００３７】この表１から、本発明の試料では、測定周波数１ｋＨｚ（室温）での比誘電率が２５００以上、絶縁破壊電圧が６０Ｖ／μｍ　以上の特性を達成できる。また、成膜１回当り０．３～０．７５μｍの膜厚で薄膜を作製できることがわかる。

【００３８】比較例１

ＭｇエトキシドとＮｂエトキシドを１：２のモル比で秤量し、２－メトキシエタノール中で還流操作（１２４℃で２４時間）を行い、ＭｇＮｂ複合アルコキシド溶液（Ｍｇ＝５ｍｍｏｌ、Ｎｂ１０ｍｍｏｌ、２－メトキシエタノール１５０ｍｍｏｌ）を合成した。

【００３９】次に酢酸鉛（無水物）１５ｍｍｏｌと１５０ｍｍｏｌの２－メトキシエタノールを混合し、１２０℃での蒸留操作により、Ｐｂ前駆体溶液を合成した。

【００４０】ＭｇＮｂ溶液とＰｂ前駆体溶液をモル比Ｐｂ：（Ｍｇ＋Ｎｂ）＝１：１になるよう混合し、室温で十分攪拌し、PMN前駆体溶液を合成した。

【００４１】イソプロポキシＴｉ（１５ｍｍｏｌ）と酢酸Ｐｂ（無水物）をモル比Ｐｂ：Ｔｉ＝１：１になるように２－メトキシエタノールに混合し、還流操作を行い、$PbTiO_3$（ＰＴ）溶液を合成した。

【００４２】合成したPMN前駆体溶液とＰＴ前駆体溶液とモル比がPMN：ＰＴ＝０．９：０．１になるよう混合し、溶液粘度６ｃＰのＰＭＮ－ＰＴ塗布溶液（溶液Ｄ）とした。また、さらに溶媒にて３倍に希釈し粘度２ｃＰの溶液Ｅを合成した。

【００４３】実施例１と同様に、電極となるＰｔ（１１１）が６５０℃でスパッタ蒸着されたサファイア単結晶基板上の上記Ｐｔ電極の表面に、溶液Ｄ、Ｅそれぞれを用いて、スピンコーターで３３００ｒｐｍ．の成膜条件で成膜し、８３０℃で１分間（大気中）の焼成を行い、膜厚０．９μｍ、０．８μｍの２種類の薄膜を得た。

【００４４】これらの溶液では、成膜１回当り、それぞれ０．０９μｍ、０．０４μｍしか作製することができず、誘電体層厚み約１．０μｍの誘電体膜を得るには、それぞれ１０回、２０回程度の成膜を必要とし、成膜効率の低いプロセスであることがわかる。得られた薄膜のＸ線回折結果より、ペロブスカイト生成率を計算するとそれぞれ約９５％であった。

【００４５】表１の試料No.２２～２５に各条件で作製した膜厚、平均粒径、平均粒径と膜厚の比、比誘電率および絶縁破壊電圧を示す。本発明の実施例と比較して、比誘電率、絶縁破壊電圧ともに劣っていることがわかる。

【００４６】

【発明の効果】以上詳述した様に、本発明によれば、平

均粒径（ｄ）と膜厚（ｔ）の比ｄ／ｔが１．０より大きい偏平粒子から構成されるＰＭＮ－ＰＴ誘電体薄膜を形成することによって、測定周波数１ｋＨｚ（室温）での比誘電率が２５００以上、絶縁破壊電圧が６０Ｖ／μｍ以上のペロブスカイト型複合酸化物結晶からなる誘電体層厚み０．３～２μｍの誘電体膜が得ることができる。これら誘電体薄膜は成膜１回当り０．３～０．７５μｍの膜厚で形成可能な成膜効率の高いプロセスを用いることにより実現できる。このような薄膜の両面に一対の電極を対向形成してコンデンサを作製することにより、測定周波数によらず高い誘電率を示し、かつ絶縁特性の良好な薄層コンデンサを実用的なプロセスで得ることができる。

【図面の簡単な説明】

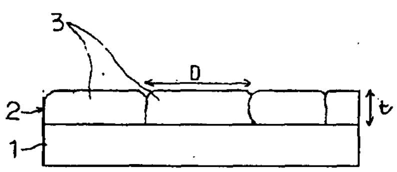
【図１】得られた誘電体薄膜を構成する結晶粒子を模式的に示した断面図である。

【図２】図１の誘電体薄膜の平面図である。

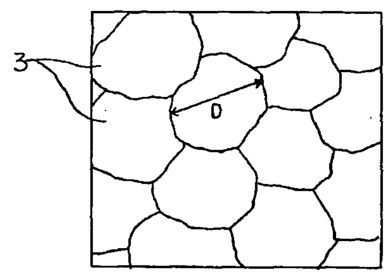
【符号の説明】

１・・・基板
２・・・誘電体薄膜
３・・・偏平粒子

【図１】



【図２】



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(71)Applicant : KYOCERA CORP

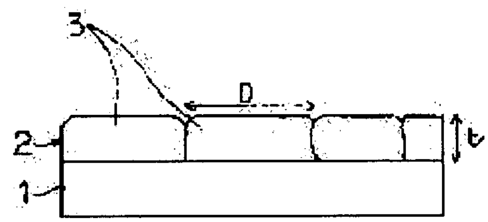
(72)Inventor : NAGAKARI HISANORI

(54) THIN DIELECTRIC FILM AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thin dielectric film having both of higher relative dielectric constant and higher insulation and a manufacturing method thereof.

SOLUTION: In a thin dielectric film 2 having a thickness of 0.3-2 μm consisting of perovskite-type crystal grains 3 containing Pb, Mg, Nb and Ti as metal elements, the perovskite-type crystal grain 3 has a grain diameter D and the film consists of flat grains 3 whose average diameter d is larger than the film thickness t. Here, the thin dielectric film 2 has a relative dielectric constant not less than 250 and a breakdown voltage not less than 60 V/μm at frequency 1 kHz (at room temperature) for measurement.



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CLAIMS

[Claim(s)]
[Claim 1] The dielectric thin film to which it is the dielectric thin film of 0.3-2 micrometers of thickness which consists of a perovskite type crystal grain child who contains Pb, Mg, Nb, and Ti as a metallic element, and the mean particle diameter d is characterized by the bird clapper by the aforementioned perovskite type crystal grain child from a larger flat particle than Thickness t.
[Claim 2] The dielectric thin film according to claim 1 characterized by for 1kHz [of test frequencies] (room temperature) specific inductive capacity being 2500 or more, and a dielectric breakdown voltage being 60v/micrometer or more.
[Claim 3] The process of the dielectric thin film characterized by producing the precursor solution of the perovskite type multiple oxide containing Pb, Mg, Nb, and Ti using the MgNb compound alkoxide molecule which has a stable Mg-O-Nb combination under existence of the organometallic compound which uses dihydric alcohol as a solvent and has other nucleophilicity, and applying, heat-treating and calcinating this precursor solution by the thickness of 0.3-0.75 micrometers on a substrate.
[Claim 4] Dihydric alcohol is the process of the dielectric thin film according to claim 3 characterized by being 1, 3-propanediol, 1, 3-butanediol, 2, and 4-pentanediol.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the dielectric thin film of the thin layer capacitor which can be especially used for DRAM and a decoupling capacitor, and its process about a dielectric thin film and its process.
[0002]
[Description of the Prior Art] In recent years, the miniaturization of electronic parts and thin film-ization are demanded with the miniaturization of electronic equipment. Especially, the formation of small large capacity of a capacitor is indispensable.
[0003] The forming-membranes methods, such as a sol gel process, a spatter, and CVD, are conventionally used as a thin film capacitor material, and it is Ta 2O5. SrTiO3 and TiO3 (Ba, Sr) Although it mainly inquired, since the specific inductive capacity of these material was small, it was difficult to realize a small mass thin film capacitor. Then, although thin film-ization of the perovskite type multiple oxide represented by Pb(Mg1 / 3 Nb 2/3) O3 which has big specific inductive capacity and the good temperature characteristic (it may be called Following PMN) is tried in order to realize these small mass thin film capacitors, the present condition is that, as for 2000 or more thin film materials, the specific inductive capacity in a room temperature is not obtained.
[0004]
[Problem(s) to be Solved by the Invention] However, the insulation of a dielectric thin film tended to become small with increase of specific inductive capacity, and, generally the insulation of the dielectric film which shows high specific inductive capacity was considered to be small. That is, the dielectric thin film material which combines high specific inductive capacity and high insulation was difficult to get.
[0005] Moreover, for the low reason, by the above-mentioned thin film formation method, the trouble [efficiency / membrane formation] of being scarce was in practicality as the technique of producing a thin film capacitor on problems, such as crack initiation.
[0006] this invention aims at offering the process which can obtain easily the dielectric thin film and such a dielectric thin film which combine high specific inductive capacity and high insulation.
[0007]
[Means for Solving the Problem] The dielectric thin film of this invention is a dielectric thin film of 0.3-2 micrometers of thickness which consists of a perovskite type crystal grain child who contains Pb, Mg, Nb, and Ti as a metallic element, and the mean particle diameter d consists [the aforementioned perovskite type crystal grain child] of a larger flat particle than Thickness t. As for a dielectric thin film, it is desirable for 1kHz [of test frequencies] (room temperature) specific inductive capacity to be [for 2500 or more and a dielectric breakdown voltage] 60v/micrometer or more.
[0008] Moreover, the dielectric thin film of this invention produces the precursor solution of the perovskite type multiple oxide containing Pb, Mg, Nb, and Ti using the MgNb compound alkoxide molecule which has a stable Mg-O-Nb combination under existence of the organometallic compound which uses dihydric alcohol as a solvent and has other nucleophilicity, and is produced by applying, heat-treating and calcinating this precursor solution by the thickness of 0.3-0.75 micrometers on a substrate. Here, as for dihydric alcohol, it is desirable that it is 1, 3-propanediol, 1, 3-butanediol, 2, and 4-pentanediol.
[0009]
[Function] At the dielectric thin film of this invention, 1kHz [of test frequencies] (room temperature) specific inductive capacity is 2500 or more, and a dielectric breakdown voltage is 60v/micrometer. The above property can be attained. This is because film insulation can be improved, in order that the number of grain boundaries may decrease in

a thin film side at the same time it discovers the high specific inductive capacity which is the feature of the large bulk object of particle size, since the crystal grain child who constitutes a dielectric layer becomes the flat particle shape from which the ratio of a mean particle diameter (d) and thickness (t) is set to d/t>1.0. Moreover, also in 100MHz of test frequencies, specific inductive capacity has 2000 or more properties, and the dielectric thin film of this invention has high specific inductive capacity also in a RF field.

[0010] And in case the dielectric thin film of this invention compounds a MgNb compound alkoxide molecule, it is set in a dihydric alcohol solvent. It also puts under existence of other nucleophilic organometallic compounds using the reaction promotion between the metallic compounds of Mg and Nb, and the technique of stabilizing a compound alkoxide molecule. The MgNb compound alkoxide which has a stable Mg-O-Nb combination is made to compound. A solution with the high viscosity containing this MgNb compound alkoxide molecule is used, and it is Pb(Mgl / 3 Nb 2/3) O3-PbTiO3 with high viscosity. A precursor solution is compounded. After applying this precursor solution on a substrate and heat-treating it by the thickness of 0.3-0.75 micrometers, the dielectric thin film of this invention can be easily obtained by calcinating.

[0011] The high specific inductive capacity in the dielectric thin film of this invention originates also in the structure of the precursor molecule in an application solution besides the factor by a crystal grain child's flat structure.

[0012] It is Pb(Mgl / 3 Nb 2/3) O3-PbTiO3, without being stable and destroying Mg-O-Nb combination to other nucleophilic organometallic compounds (for example, lead acetate), since the MgNb compound alkoxide molecule which already has the structure near a cholane byte (MgNb 2O6) in the stage of a solution and which has a firm Mg-O-Nb combination is formed. Since a precursor is formed, high specific inductive capacity is realized.

[0013] Moreover, since the thickness per membrane formation increased by the increase in viscosity of an application solution, the flat particle in the dielectric thin film of this invention is generated. This is because the grain growth after crystallization grows as a flat particle with a large particle size to the thickness which generated within the film surface and was shown above while the concentration of the precursor which exists in the film becomes high and formation of 0.3-0.75 micrometers [per membrane formation] thickness is attained for increase of application thickness. Moreover, generation of a flat particle enables it to obtain the dielectric thin film which has the high insulation of a 60v [/micrometer] dielectric breakdown voltage, in order that the number of the grain boundaries may decrease.

[0014]

[Embodiments of the Invention] The dielectric thin film of this invention is characterized by consisting of flat particles. The cross section and drawing 2 which show the state where drawing 1 formed the dielectric thin film 2 on the substrate 1 show the plan, and the particle 3 of particle size D exists in the dielectric thin film 2 of Thickness t. here -- the ratio of a mean particle diameter (d) and thickness (t) -- the case where d/t was larger than 1.0 was defined as a flat particle 3 In especially the dielectric thin film of this invention, four or more flat particles 3 to a bird clapper has [two or more] desirable d/t for specific inductive capacity and the improvement in insulation resistance.

[0015] In dielectric thin film production of this invention, the precursor solution which the organometallic compound of Pb, Mg, Nb, and Ti dissolved uniformly as an application solution first is prepared.

[0016] The organic acid chloride of Mg and Nb, mineral salt, at least one sort of Mg compounds chosen from an alkoxide, and Nb compound are first mixed to the alcoholic divalent solvent shown by the mole ratio of Mg:Nb=1:2 by R(OH)2 and the three or more R:carbon numbers alkyl group.

[0017] Reflux operation is performed after mixture and the MgNb compound alkoxide molecule which has a stable Mg-O-Nb combination under existence of other nucleophilic organometallic compounds is compounded.

[0018] If the ethylene glycol of a carbon number 2 is used as a solvent at this time, the bridge formation effect of a solvent will be promoted and nebula and gelling will arise. In order to think the stability of an application solution as important, the molecular structure of a dihydric alcohol solvent molecule is important, and it is desirable to choose solvents, such as 1 which takes 6 member ring structure and has stabilization effect according to alcoholic exchange reaction with MgNb compound alkoxide molecule which had and compounded hydroxyl group in 1, 3 and 2, and 4 position in molecule, 3-propanediol, 1, 3-butanediol, 2, and 4-pentanediol.

[0019] Moreover, in order to obtain the MgNb compound alkoxide molecule which has a stable Mg-O-Nb combination, there are the following methods. (1) How to promote a ** ester reaction within a molecule by reflux operation with the carboxylate of Mg, and the alkoxide of Nb. (2) How to add the stabilizing agent represented by an acetic anhydride, an ethanolamine, the acetylacetone, etc., after mixing the alkoxide raw material of Mg and Nb to a solvent, raising the temperature of a solution to the boiling point of a solvent and performing composite-ization by reflux operation. (3) Promote a dealcoholization reaction within a molecule by reflux operation of the hydroxide of Mg, the alkoxide of Nb or the alkoxide of Mg, and the hydroxide of Nb.

[0020] Although the MgNb compound alkoxide molecule which has a stable Mg-O-Nb combination under existence of other nucleophilic organometallic compounds by using one technique of more than is compoundable, especially the

method of (1) is desirable also among these.
[0021] Next, at least one sort of lead compounds chosen from leaden (Pb) organic acid chloride, mineral salt, and an alkoxide are mixed in the above-mentioned Mg-Nb compound solution, and it considers as the PMN application solution which consists of a mole ratio of Pb:(Mg+Nb) =1:1. At this time, you may make Pb into an excess several%.
[0022] When raising the viscosity of a solution furthermore, you may perform heating polymerization operation at 90 to 100 degrees C. By this heating polymerization, the application solution which has the high solution viscosity of several 100 or more cPs can be obtained.
[0023] PbTiO3 (PT) precursor solution mixes at least one sort of lead compounds chosen from leaden (Pb) organic acid chloride, mineral salt, and an alkoxide, at least one sort of titanium compounds chosen from the organic acid chloride of titanium (Ti), mineral salt, and an alkoxide, and a dihydric alcohol solvent, and is obtained by performing reflux operation. In this case, solution viscosity can obtain the solution of 50cP-100cP.
[0024] A PMN-PT precursor solution is obtained by mixing the PMN precursor solution and PT precursor solution which were compounded previously. Although the solution viscosity after mixing is based also on the viscosity of a PMN solution, they are about 1200 cP(s) from solution viscosity 70cP.
[0025] Membranes are formed by technique, such as the spin coat method, a dip coating method, and a spray method, on the substrate in which the lower electrode was formed using the these-produced PMN-PT application solution.
[0026] After membrane formation, after drying at the temperature of 100 degrees C or less, it heat-treats at the temperature of 300 degrees C - 400 degrees C, the organic substance which remained in the film is burned, and it considers as a gel film. The dryness process 100 degrees C or less is required in order to prevent crack initiation in the stage of a gel film.
[0027] A gel film without the obtained crack is calcinated at 750 degrees C - 850 degrees C, and the dielectric thin film of a crystalline substance is produced. Although the thickness of the obtained dielectric thin film is based also on the viscosity and the membrane formation conditions of a solution which were used, it is 0.3-0.75 micrometers per membrane formation. When enlarging a bed depth furthermore, membrane formation operation is repeated. However, in order to suppress the crack initiation after baking, it is required for the thickness after baking to be 2.0 micrometers or less. Moreover, when an insulating property is taken into consideration, the crystal grain child in a dielectric layer has the desirable organizations which consist of flat particles whose particle size is 0.5-2 micrometers.
[0028] The thin film capacitor of this invention forms Pt, Au, Cr, nickel, Cu, etc. by technique, such as a spatter, a vacuum deposition, and gravure, on the substrate chosen from an alumina, sapphire, Si, etc., and forms a lower electrode. Although there is especially no limit in the surface roughness of a substrate at this time, in order to prevent the crack initiation of the film by bulging in an electrode-substrate interface, it is important to raise the adhesion between electrode-substrates.
[0029] The above-mentioned dielectric film is formed and formed in the front face of this lower electrode layer by the above-mentioned method, and it is obtained by forming an up electrode as well as a lower electrode on a dielectric thin film front face next. Moreover, a multilayer capacitor is obtained by carrying out the laminating of a dielectric layer and the electrode by turns.
[0030]
[Example]
Weighing capacity of the example 1 acetic acid Mg and the Nb ethoxide was carried out by the mole ratio of 1:2, reflux operation (it is 6 hours at 124 degrees C) was performed in 1 and 3-propanediol, and the MgNb compound alkoxide solution (Mg=5mmol, Nb10mmol, 1, 3-propanediol 150mmol) was compounded. Next, mixed lead acetate 3 hydrate 15mmol so that it might be set to mole-ratio Pb:(Mg+Nb) =1:1, and it was made to dissolve by heating at 60 degrees C for 25 minutes, and the PMN solution was compounded.
[0031] Isopropoxy Ti (15mmol) and an acetic acid Pb (anhydride) are mixed to 1 and 3-propanediol so that it may be set to mole-ratio Pb:Ti=1:1, reflux operation is performed, and it is PbTiO3. The (PT) solution was compounded.
[0032] It mixed so that the compound PMN precursor solution and compound PT precursor solution, and a mole ratio might be set to PMN:PT=0.9:0.1, and it considered as the PMN-PT application solution (solution A) of solution viscosity 130cP.
[0033] The heating polymerization of the application solution A was carried out at 90 degrees C, and solution viscosity 300cP (solution B) and solution viscosity 560cP (solution C) were compounded, respectively.
[0034] After Pt (111) used as an electrode applied the three aforementioned sorts of application solutions (solutions A, B, and C) to the front face of the above-mentioned Pt electrode on the sapphire single crystal substrate by which spatter vacuum evaporationo was carried out, and an alumina substrate, respectively and made it dry them by the membrane formation conditions of 2500rpm., 3300rpm., and 5000rpm. at 650 degrees C at a spin coater, it heat-treated at 300 degrees C, and the gel film without a crack was produced. Then, baking for 3 minutes (inside of the atmosphere) was

performed at 830 degrees C. Moreover, it restricted to the sample which a crack did not generate after one membrane formation, the above-mentioned operation was repeated 2 times and 3 times, and the sample which thickened thickness was also produced.

[0035] Then, using the LCR meter (HP4284made from Hewlett Packard A), the electrostatic capacity of a thin film capacitor was measured and it asked for specific inductive capacity. Using picoampere meter (HP4140made from Hewlett Packard B), the dielectric breakdown voltage impressed the direct current voltage of 0V to 100V, and evaluated the time of a leakage-current value becoming more than 1x10-3A as dielectric breakdown. The mean particle diameter (d) was computed from the SEM observation photograph on the front face of a thin film using the intercepting method. Moreover, thickness (t) was computed from the cross-section SEM observation photograph of a thin film. These results were indicated to Table 1.

[0036]

[Table 1]

試料 No.	溶液 No.	溶液粘度 (cP)	成膜条件 (rpm.)	塗布膜厚 μm/回	塗布回数	膜厚 t μm	平均粒径 d μm	d/t	比誘電率	絶縁破壊電圧 V/μm	備考
1	A	130	5000	0.30	1	0.30	3.3	11.0	3100	85	
2	A	130	5000	0.30	2	0.63	3.6	5.7	3200	80	
3	A	130	5000	0.30	3	0.9	3.8	4.2	3100	75	
4	A	130	3300	0.4	1	0.4	2.5	6.3	3000	77	
5	A	130	3300	0.4	2	0.8	2.8	3.5	3100	70	
6	A	130	3300	0.4	3	1.2	3.0	2.5	3100	70	
7	A	130	2500	0.65	1	0.65	1.4	2.2	2700	67	
8	A	130	2500	0.65	2	1.2	1.8	1.5	2700	65	
9	A	130	2500	0.65	3	2.0	2.3	1.2	2800	65	
10	B	300	5000	0.4	1	0.4	2.5	6.3	3000	75	
11	B	300	5000	0.4	2	0.7	2.8	4.0	3100	75	
12	B	300	5000	0.4	3	1.15	3.1	2.7	3000	70	
13	B	300	3300	0.6	1	0.6	2.1	3.5	3050	70	
14	B	300	3300	0.6	2	1.15	2.4	2.1	3100	65	
15	B	300	3300	0.6	3	1.7	2.6	1.5	3100	60	
16	C	560	5000	0.55	1	0.55	1.2	2.2	2700	67	
17	C	560	5000	0.55	2	1.0	1.4	1.4	2600	65	
18	C	560	5000	0.55	3	1.45	1.6	1.1	2700	60	
19	C	560	3300	0.75	1	0.75	1.2	1.6	2800	65	
20	C	560	3300	0.75	2	1.3	1.6	1.2	2800	60	
*21	C	560	3300	0.75	3	2.1	2.3	1.2	-	-	クラック
*22	D	6	3300	0.09	10	0.9	0.4	0.44	2000	45	
*23	E	2	3300	0.04	20	0.8	0.3	0.38	1800	40	
*24	D	6	3300	0.09	4	0.36	0.2	0.56	1900	50	
*25	D	6	3300	0.09	3	0.27	0.15	0.56	1800	47	

*印は本発明の範囲外の試料を示す。

[0037] At the sample of this table 1 to this invention, 1kHz [of test frequencies] (room temperature) specific inductive capacity is 2500 or more, and a dielectric breakdown voltage is 60v/micrometer. The above property can be attained. Moreover, it turns out that a thin film is producible by 0.3-0.75 micrometers [per membrane formation] thickness.

[0038] Weighing capacity of example of comparison 1Mg ethoxide and the Nb ethoxide was carried out by the mole ratio of 1:2, reflux operation (it is 24 hours at 124 degrees C) was performed in the 2-methoxyethanol, and the MgNb compound alkoxide solution (Mg=5mmol, Nb10mmol, 2-methoxyethanol 150mmol) was compounded.

[0039] Next, the 2-methoxyethanol of lead acetate (anhydride) 15mmol and 150mmol(s) was mixed, and Pb precursor solution was compounded by distillation operation at 120 degrees C.

[0040] The MgNb solution and Pb precursor solution were mixed so that it might be set to mole-ratio Pb:(Mg+Nb) =1:1, and it agitated enough at the room temperature, and the PMN precursor solution was compounded.

[0041] Isopropoxy Ti (15mmol) and an acetic acid Pb (anhydride) are mixed to a 2-methoxyethanol so that it may be set to mole-ratio Pb:Ti=1:1, reflux operation is performed, and it is PbTiO3. The (PT) solution was compounded.

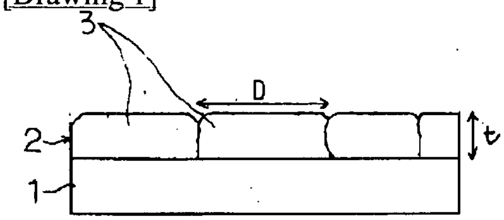
[0042] It mixed so that the compound PMN precursor solution and compound PT precursor solution, and a mole ratio

might be set to PMN:PT=0.9:0.1, and it considered as the PMN-PT application solution (solution D) of solution viscosity 6cP. Furthermore, it diluted with the solvent 3 times and the solution E of viscosity 2cP was compounded.
[0043] the front face of the above-mentioned Pt electrode on the sapphire single crystal substrate to which the spatter vacuum evaporationo of the Pt (111) used as an electrode was carried out at 650 degrees C like the example 1 -- Solutions D and E -- using each, membranes were formed on the membrane formation conditions of 3300rpm. by the spin coater, baking for 1 minute (inside of the atmosphere) was performed at 830 degrees C, and the thickness of 0.9 micrometers and two kinds of 0.8-micrometer thin films were obtained
[0044] With these solutions, in order to be able to produce only 0.09 micrometers and 0.04 micrometers, respectively but to obtain the dielectric film which is the dielectric-layer thickness of about 1.0 micrometers per membrane formation, 10 times and about 20 membrane formation are needed, respectively, and it turns out that it is the low process of membrane formation efficiency. When the perovskite yield was calculated from the X diffraction result of the obtained thin film, it was about 95%, respectively.
[0045] The ratio of the thickness produced on each conditions to sample No.22-25 of Table 1, a mean particle diameter, a mean particle diameter, and thickness, specific inductive capacity, and a dielectric breakdown voltage are shown. As compared with the example of this invention, it turns out that specific inductive capacity and the dielectric breakdown voltage are inferior.
[0046]
[Effect of the Invention] according to [as explained in full detail above] this invention -- the ratio of a mean particle diameter (d) and thickness (t) -- a dielectric film with a dielectric-layer thickness of 0.3-2 micrometers which 2500 or more and a dielectric breakdown voltage become [1kHz / of test frequencies / (room temperature) specific inductive capacity] from a 60v [/] or more perovskite type multiple-oxide crystal micrometer can obtain by forming the PMN-PT dielectric thin film by which d/t is constituted from a larger flat particle than 1.0 These dielectrics thin film is realizable by using the high process of the membrane formation efficiency which can be formed by 0.3-0.75 micrometers [per membrane formation] thickness. By carrying out opposite formation of the electrode of a couple at both sides of such a thin film, and producing a capacitor, it is not based on a test frequency, but a high dielectric constant can be shown and the good thin layer capacitor of an insulating property can be obtained in a practical process.

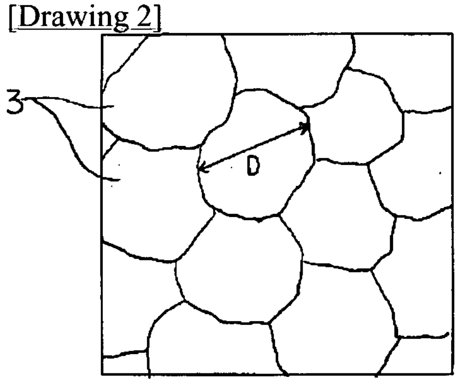
[Translation done.]

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]